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Degradation of Diclofenac and 3-Amine-5-Methylisoxazole by a Homogeneous Solar Photo-Fenton Process Mediated by Ferrioxalate Complexes

ABSTRACT

Environmental protection is one of the great challenges of this century, being one of the most discussed topics that mobilized the world's population to the issue of socio-environmental responsibility. The lack of sanitation, untreated industrial wastewaters discharge and ineffective wastewater treatment plants (WWTP) enhanced the problem of water contamination. Diclofenac (DCF) is a nonsteroidal anti-inflammatory drug commonly used as analgesic and frequently detected in aquatic environments, suggesting a continuous significant input of DCF into the ecosystem, mainly associated to the ineffectiveness of traditional WWTPs. Sulfonamides or sulfa drugs are the basis of several groups of drugs that contain organic nitrogen species in their structure. Various studies have identified 3-amino-5-methylisoxazole (AMI) as a byproduct of sulfamethoxazole (SMX) degradation, a commonly prescribed sulfa antibiotic, and some authors have reported the accumulation of AMI during the biodegradation of SMX in stoichiometric proportion to the parent compound.

Tertiary/quaternary advanced methods have been evaluated to deal with this environmental concern, including advanced oxidation processes (AOPs), an environmental sound technology characterized by the production of reactive oxygen species, such as hydroxyl radicals ($\cdot\text{OH}$), which are one of the most reactive species known in the environment. The high costs associated with energy and chemicals consumption has led to the development of systems using renewable solar energy to promote the oxidation process, such as the solar photo-Fenton process.

In this work, a solar photo-Fenton enhanced process mediated by ferrioxalate (SPFF) was used for the degradation of two emerging pollutants, DCF and AMI. For DCF experiments, SPFF was used at low iron concentrations and near neutral pH conditions, avoiding DCF and iron precipitation, using artificial and natural solar radiation in CPCs photoreactors, at lab and pilot plant scale. The effect of different process variables, such as, temperature (15-45°C), pH (5.0 and 6.0), UVA irradiance (27.8 - 59.9 $\text{W}_{\text{UV}}/\text{m}^2$), presence of inorganic ions (0.1 g/L; Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ and HCO_3^-) and radical scavengers (sodium azide and D-mannitol), DCF initial concentration (2, 5, 10 and 20 mg L^{-1}), Fe^{3+} concentration (1 and 2 mg L^{-1}) and iron/oxalate molar ratio (1:3, 1:6 and 1:9) was evaluated. The efficiency of the SPFF was also compared with different chemical (H_2O_2), catalytic ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$), photochemical (UVA, $\text{H}_2\text{O}_2/\text{UVA}$) and photocatalytic processes ($\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UVA-Vis}$). For AMI experiments, the main goal was to investigate antibiotic degradation by means of SPFF and conventional solar photo-Fenton (CSPF) processes. The SPFF process was assessed at different iron/oxalate molar ratios (1:3; 1:6 and 1:9), total dissolved iron concentration of 2.0 $\text{mg Fe}^{3+} \text{ L}^{-1}$ (0.036 mM) and pH range of 3.5 – 6.5. The CSPF method was evaluated at total dissolved iron amount of 2.0 $\text{mg Fe}^{2+} \text{ L}^{-1}$ and pH range of 2.8 – 4.0. Modified photo-Fenton reaction was also evaluated using other organic ligands, such as citrate acid and ethylenediamine-N,N'-disuccinic acid (EDDS). Moreover, DCF and AMI degradation and mineralization profiles were also evaluated in a pilot plant with CPCs, using the best conditions obtained at lab-scale. DCF and AMI mineralization was assessed in terms of Dissolved Organic Carbon (DOC), low-molecular-weight carboxylate ions and inorganic ions present in the solution.

Process intensification of a solar photo-Fenton reaction with ferrioxalate complexes showed promising results in the elimination of diclofenac at lab and pilot scale, as a model compound of emerging pollutants, at near neutral pH conditions, avoiding the precipitation of DCF and

ferric hydroxides, and using low iron concentrations ($[\text{Fe}^{3+}] \leq 2 \text{ mg L}^{-1}$). The photo-Fenton reaction mediated by ferrioxalate complexes enhances significantly the DCF removal rates and reduces H_2O_2 consumption, mainly because the conventional photo-Fenton reaction is characterized by i) a slow DCF precipitation-redissolution-degradation mechanism under acidic conditions; and ii) DCF degradation via a ligand-to-metal charge mechanism that occurs on the surface of the iron precipitates, under neutral pH conditions. To achieve complete DCF removal, i.e. concentrations below the detection limit, after 90 min of reaction ($T = 25 \text{ }^\circ\text{C}$ and $I = 41.6 \text{ W}_{\text{UV}} \text{ m}^{-2}$), iron/oxalate molar ratios of 1:3 at pH 5.0 and 1:9 at pH 6.0 were required, resulting in 55% and 63% mineralization, consuming 2.0 and 1.9 mM H_2O_2 , respectively.

The degradation of AMI by SPFF and CSPF processes in aqueous solution showed promising results both at lab and pilot-scale. The SPFF process made possible to study AMI removal at near neutral pH. Results showed that an iron/oxalate molar ratio of 1:9 ($[\text{Total iron}] = 3.58 \times 10^{-2} \text{ mM}$; $[\text{Oxalic acid}] = 3.22 \times 10^{-1} \text{ mM}$) was necessary to remove 72.0% of AMI, although no DOC removal was observed after 90 min of reaction. At pH 3.5, an iron/oxalate molar ratio of 1:3 ($[\text{Total iron}] = 3.58 \times 10^{-2} \text{ mM}$; $[\text{Oxalic acid}] = 1.07 \times 10^{-1} \text{ mM}$) was enough to achieve complete degradation of the AMI solution (below the detection limit) and 30% mineralization after 30 min (with 45% DOC removal in 90 min), consuming 1.0 mM H_2O_2 . Ferric-organic ligands citrate acid and EDDS at pH 5.0 do not differ appreciably from the ferrioxalate complexes. Promising results were observed applying the CSPF. Low iron concentrations of 2.0 mg L^{-1} and pH 3.5 were sufficient to achieve complete removal of 20 mg L^{-1} AMI and 35% mineralization after 40 min ($1.6 \text{ kJ}_{\text{UV}} \text{ L}^{-1}$), with 1.25 mM of H_2O_2 consumption.

The presence of inorganic ions, such as sulfate, chloride, nitrate, ammonium and bicarbonate, in a concentration of 0.1 g L^{-1} , temperature ($15\text{-}45^\circ\text{C}$) and irradiance ($27.8\text{-}59.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$), did not influence significantly the DCF reaction rates. On the other hand, the presence of 0.1 g L^{-1} inorganic ions slightly reduced the AMI reaction rates, with an order of interference as $\text{NO}_3^- < \text{NH}_4^+ < \text{SO}_4^{2-} < \text{HCO}_3^-$. AMI removal was accelerated in the presence of chloride ion possibly due to the formation of AMI-Cl complexes, avoiding the formation of AMI-Fe(III) complexes. Radical scavengers, sodium azide 10 mM (NaN_3) and D-mannitol 50 mM showed strong interference in DCF and AMI removal, suggesting that $\cdot\text{OH}$ play an important role in degradation process. Although degradation was mainly attributed to hydroxyl radicals, other radical species formed during the photodecarboxylation of ferrioxalate complexes also can play an important role. Both AMI and DCF degradation kinetics followed a pseudo-first-order model for all conditions tested.

Pilot plant assays were performed under natural solar radiation and the best SPFF lab-scale condition ($[\text{DCF}]_0 = 20 \text{ mg L}^{-1}$, pH 5.0, iron/oxalic molar ratio of 1:3, $[\text{Fe}^{3+}] = 2.0 \text{ mg L}^{-1}$). A detailed assessment of the formation of low-molecular-weight carboxylic acids and inorganic ions suggests that after the point of complete DCF abatement the remaining organic compounds are mainly attributed to biodegradable acetic acid. Acetic acid forms a stable complex with ferric ions, which has a low photoactivity under UVA-visible light, and acetic acid is very resistant to the attack of hydroxyl and other reactive oxygen species, stopping the photo-Fenton reaction. AMI degradation kinetic at pilot plant scale was done under natural solar radiation conditions using CSPF at pH 3.5 and results showed a good reproducibility to those obtained in the lab-scale photoreactor. The nitrogen atom presents in the AMI molecule structure was released as ammonium, nitrite and nitrate ions. Oxalic and oxamic acids were identified as the main low-molecular-weight carboxylic acids detected during the CSPF reaction.

Results obtained in this work showed that SPFF and CSPF processes can be an interesting alternative to remove nitrogenated organic pollutants that cannot be treated by conventional biological methods. Since no studies on AMI degradation by AOPs were done before, this work can be used as reference for future studies using this compound, since we presented a wide range of experiments and results.